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STRESS CORROSION CRACKING OF TITANIUM ALLOYS

PROGRESS REPORT: JULY 1 - SEPTEMBER 30, 1964

S. P. Rideout, M. R. Louthan, Jr., and C. L. Selby

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STRESS CORROSION CRACKING OF TITANIUM ALLOYS

PROGRESS REPORT: JULY 1 - SEPTEMBER 30, 1964

by

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ABSTRACT

Work was continued to determine the mechanism of stress corrosion cracking of titanium alloys exposed to hot chloride salts.

Metallographically polished strips of Ti-8Al-1Mo-1V alloy that were stressed to the yield point at 650°F cracked within 3-1/2 hours with a maximum depth of 0.022 inch after 14 days. A heavy oxide film appears to inhibit cracking.

Additional evidence was obtained indicating that HCl gas and presumably NaOH are formed during dehydration of sea salt; either or both may be involved in the corrosion.

Oxides formed at 900 and 1100°F on 8-1-1 alloy are enriched with aluminum. Cracking may involve selective attack of this alloying element by NaOH or NaCl.

Of the four principal chlorides in sea salt, NaCl and KCl used individually caused much more cracking than $MgCl_2$ or $CaCl_2$. The difference may be related to the relative strengths of the hydroxides of the cations. Radiotracers ^{22}Na and ^{36}Cl in sea salt are being used to study the roles of sodium and chlorine in the corrosion reactions. Traces of both were detected on cracked samples.

Transmission electron microscopy studies of the Ti-8Al-1Mo-1V alloy were continued.

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STRESS CORROSION CRACKING OF TITANIUM ALLOYS

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INTRODUCTION

This is the second quarterly progress report of NASA-sponsored research by the Savannah River Laboratory on the mechanism of hot-salt stress corrosion cracking of titanium alloys.

The objective of this research is to develop fundamental knowledge about the corrosion phenomena involved in cracking. Emphasis is being placed on study of the Ti-8Al-1Mo-1V alloy because it is a prime candidate as a structural material for the proposed supersonic transport aircraft (SST). This alloy is known to be susceptible to hot-salt cracking in laboratory tests under conditions that may occur during operation of the SST, i.e., skin temperature in the range of 550-650°F with salt contamination acquired during transoceanic operations.

Radioactive tracer elements are being used in studies of the chemical reactions that occur during initiation and propagation of cracks. Electron microscopy techniques are being used to study crack morphology and to determine the effects of heat treatment and alloy structure on cracking.

Some incomplete or unconfirmed data may be included in these progress reports.

SUMMARY

REVIEW OF FIRST QUARTER

Tests performed during the first quarter⁽¹⁾ indicated that heating sea salt alone to 650°F produced a volatile chloride-bearing product believed to be HCl gas formed by dehydration. It was suggested that either the HCl gas or resultant hydroxides remaining in the salt may be involved in the initiation of stress corrosion cracking.

"Salt sandwiches" made by clamping individual salt crystals between strips of Ti-8Al-1Mo-1V alloy were heated 8 hours at temperatures from 400 to 1200°F in an attempt to observe the salt-metal reaction and obtain corrosion products for identification analyses. Visible corrosion products formed at temperatures >800°F.

Electron microscopy studies revealed that:

- Cracks propagate along alpha phase grain boundaries and alpha-beta phase interfaces.
- Cracks formed at 1200°F appeared to propagate by chemical attack with no evidence of mechanical rupture.
- The beta phase is cathodic to the alpha matrix.

Thin foils of the Ti-8Al-1Mo-1V alloy were successfully prepared for electron transmission studies of fine structure.

SUMMARY OF SECOND QUARTER

Stress corrosion cracking initiated very rapidly in metallographically polished strips of Ti-8Al-1Mo-1V alloy stressed to the yield point and heated at 650°F. Cracks were visible after 3-1/2 hours; the maximum crack depth in a duplex-annealed specimen after 14 days was 0.022 inch. An apparent difference in crack propagation rate was observed in two heats of the same alloy, one of which was mill-annealed and one-duplex annealed. Cracks propagated faster in the duplex-annealed alloy.

Microscopic examination of salt contact spots on polished surfaces indicated that the oxide film was thinner in the area surrounding the spots (Figure 3). The oxide film on the titanium alloy appears to protect against initiation of stress corrosion. A flame-oxidized sample had only three small cracks after 14 days at 650°F, whereas samples with a polished surface had numerous cracks after the same exposure.

The composition of the titanium oxide film is being studied to determine if selective attack of alloying elements is involved in stress corrosion cracking. Preliminary analyses by spark-source mass spectrometer of films formed at 900 and 1100°F suggest that the ratio of aluminum to titanium is greater in the oxide than in the base metal (Table II).

Confirming evidence was obtained that HCl gas is given off during sea salt dehydration, and that most of the HCl gas is released during the first few hours of heating at 650°F (Figure 4). The possibility that HCl gas or resultant hydroxide in the salt is involved in the initiation of stress corrosion is being investigated.

Tests comparing the degree of cracking caused by each of the four principal salts in sea salt (NaCl , KCl , MgCl_2 , and CaCl_2) showed that NaCl and KCl produced severe cracking during two weeks exposure at 650°F , while MgCl_2 and CaCl_2 produced only a few tiny cracks (Figure 5). This may be related to the fact that sodium and potassium form strong hydroxides while magnesium and calcium form weak hydroxides.

Attempts to identify the corrosion products of sea salt and Ti metal have been unsuccessful. In order to reduce the complexity of corrosion products, pure NaCl , which has been demonstrated to be an effective cracking agent, will be used instead of sea salt for future tests.

Separate tests using salt containing radiotracer ^{36}Cl and salt containing radiotracer ^{22}Na showed that small amounts of both ^{36}Cl and ^{22}Na were present in cracked areas (Table III). An autoradiographic technique is being investigated, but has not yet been perfected, to determine the exact location of these radiotracers with respect to the cracks.

In duplex-annealed sheet material, the initiation of stress corrosion cracks appears to be independent of the orientation of the sample with respect to the rolling direction. Room-temperature tensile tests of this material also showed no significant differences of mechanical properties or strain anisotropy in the longitudinal and transverse directions.

Transmission electron microscopy of thin foils of duplex-annealed Ti-8Al-1Mo-1V alloy showed that the matrix was alpha phase and that the large second-phase particles were beta phase. Structural features such as dislocations, dislocation networks, and stacking faults were observed in many areas in the foil, suggesting that the stacking fault energy of the alloy was rather low.

DISCUSSION

PROCUREMENT

A 4- by 8-foot sheet of 0.050-inch-thick Ti-8Al-1Mo-1V alloy was received from Langley Research Center. Sheet from the same heat, number D-5657, was used by Langley for studies of mechanical properties. This material was used in most of the tests during the second quarter and will be used in all future tests.

Radiotracer ^{22}Na (as NaCl acidic solution) was purchased from Oak Ridge for studies of the role of sodium in the stress corrosion phenomenon. This isotope emits both beta and gamma radiation as follows:

$$^{22}\text{Na} \text{ half-life} = 2.58 \text{ years}$$

$$\beta^+ = 0.54 \text{ Mev}$$

$$\gamma = 1.28 \text{ Mev}$$

This radiotracer was incorporated into a neutral saturated solution of NaCl.

EXPERIMENTAL PROCEDURE

The initiation and propagation of hot-salt cracking was studied using metallographically polished strips of Ti-8Al-1Mo-1V alloy. Two different heats of the alloy were used: TMCA D-3420 (0.030-inch sheet, mill-annealed), and TMCA D-5657 (0.050-inch sheet, duplex-annealed). Heat analyses are given in Table I. In order to obtain results in a reasonable time, tests were performed at 650°F with samples stressed to the yield point.

TABLE I
Heat Analyses of Ti-8Al-1Mo-1V Alloy

| Element | Composition, wt % | |
|---------|---|---|
| | Heat No. D-3420 (0.030-inch sheet, mill-annealed) | Heat No. D-5657 (0.050-inch sheet, duplex-annealed) |
| C | 0.023 | 0.026 |
| Fe | 0.08 | 0.11 |
| N | 0.012 | 0.011 |
| Al | 7.7 | 7.9 |
| V | 1.0 | 1.0 |
| Mo | 1.0 | 1.1 |
| H | 0.006-0.007 | 0.003-0.006 |

Strips 3/4 inch by 3 inches were ground and polished on one surface, then stressed in a four-point loading sample holder to a calculated stress of 90,000 to 100,000 psi at room temperature. Salt was applied as droplets of a saturated neutral solution. Various forms of salt were used: natural sea salt, sea salt containing ^{36}Cl , NaCl containing either ^{22}Na or ^{36}Cl , and individual chlorides of K, Mg, and Ca. The samples were placed in a small muffle furnace at 250°F to dry the salt, then transferred to a muffle furnace at 650°F and exposed for various times up to 49 days. The stress level at 650°F was apparently at the yield point because the strips were slightly bowed when removed from the sample holders.

The strips were examined microscopically after the salt deposits were removed by swabbing in running water. Representative samples were sectioned to determine depth of cracking, while the remaining samples were studied by radiation counting techniques and/or autoradiography to determine the roles of chloride and sodium. In some cases the corroded surfaces were reground and repolished to determine if radiotracers remained in the cracked areas.

A few U-bend samples stressed to plastic yield were also exposed at 650°F for metallographic examinations.

EXPERIMENTAL RESULTS

Initiation and Propagation of Cracking

Stress corrosion cracking initiated very rapidly in metallographically polished surfaces. Tiny cracks were observed microscopically at points of contact with NaCl crystals on one sample from heat D-5657 after only 3-1/2 hours as illustrated in Figure 1. Incipient cracking of samples from heat D-3420 was also detected under deposits of sea salt after 5 hours.

Crack depths were measured on metallographic sections of samples from heat D-3420 (mill-annealed) exposed for periods of 1 to 49 days and are plotted in Figure 2. Maximum crack depth was 0.005 inch after 1 day and 0.010 inch after 49 days. No measurements were made on cracks that formed in less than 1 day, but the fact that cracks were visible on the surface after 5 hours indicates that the incubation period for cracking is less than 5 hours. The rate of crack propagation in these four-point loaded strip samples was much slower than in U-bend type samples of the same heat (D-3420) also exposed at 650°F. After 14 days, the depth of cracking in U-bend samples was 0.020 to 0.025 inch. This difference in crack propagation rate is probably due to the combination of cold work of the metal during bending into the U-shape and the more complex stress patterns developed in the U-bend samples.

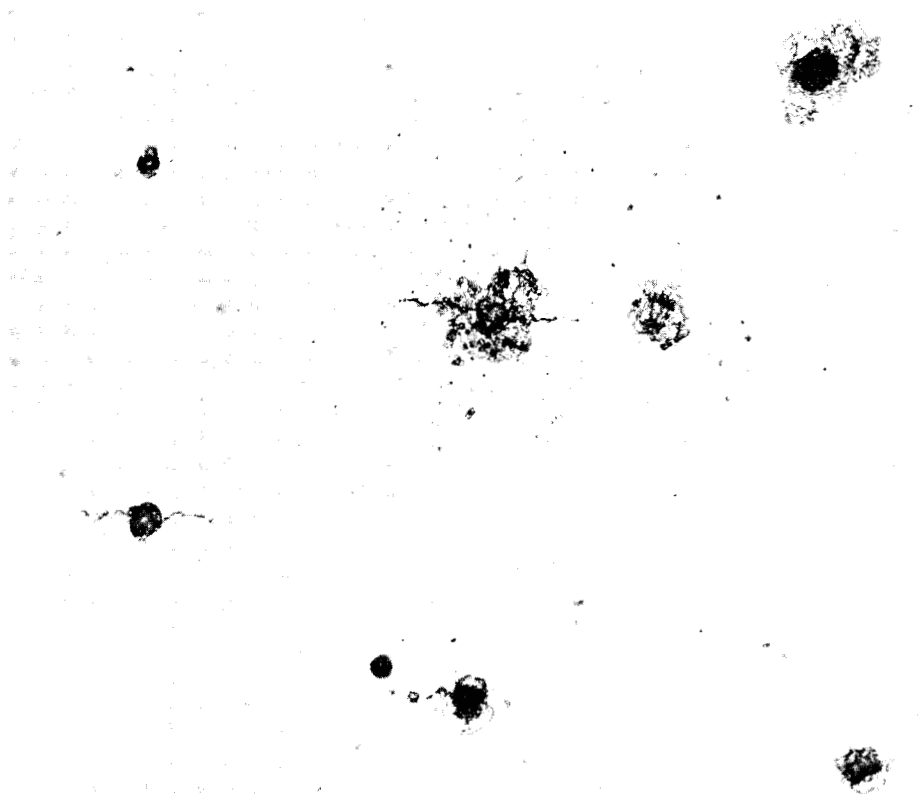


FIG. 1 MICROCRACKS AT NaCl CONTACT SPOTS ON PREPOLISHED Ti-8Al-1Mo-1V ALLOY AFTER 3½ HOURS AT 650°F. Sample was duplex-annealed material, stressed to the yield stress at 650°F. 250X

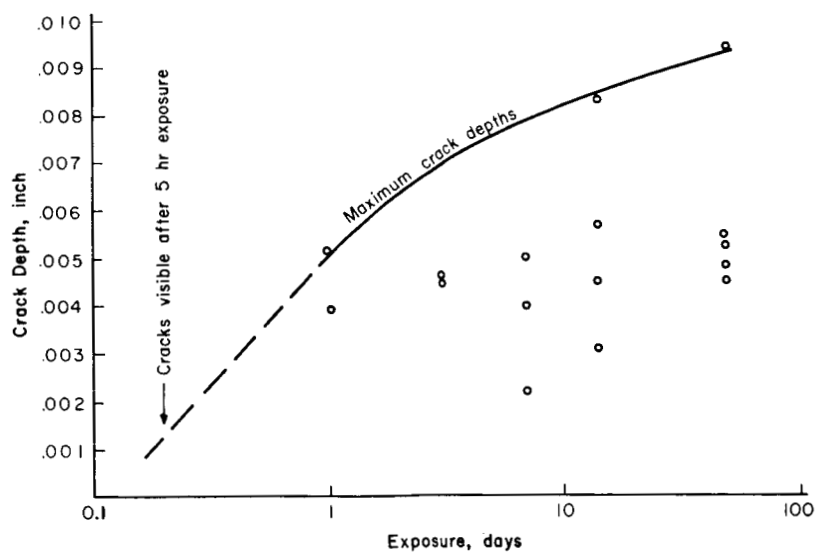


FIG. 2 CRACK DEPTH IN MILL-ANNEALED Ti-8Al-1Mo-1V ALLOY STRIP, STRESSED TO YIELD AT 650°F WITH SEA SALT DEPOSITS

The factors that influence the crack propagation rate have not been investigated in detail, but the propagation rate in the duplex-annealed heat D-5657 was greater than in the mill-annealed heat D-3420. In four-point-loaded strip samples from D-5657 the maximum crack depth was 0.022 inch after 14 days at 650°F.

The effects of alloy composition, cold work, heat treatments, stress level, and test temperature on the time to initiate cracking and the rate of propagation will be investigated in future tests.

Examination of Salt Contact Spots

Microscopic examination of sample surfaces after the excess salt had been removed revealed several interesting features. Figure 3 shows the surface of a sample exposed 1 day at 650°F to a deposit of sea salt that was applied initially as droplets of a saturated solution. Spots where individual salt crystals reacted with the metal were clearly visible. Pitting and cracking occurred at many of these spots. An unusual pattern of corrosion shown in area "B" appeared to be related to some crystallographic feature of the salt crystal. The pattern was much larger than the size of the individual grains in the metal, as is

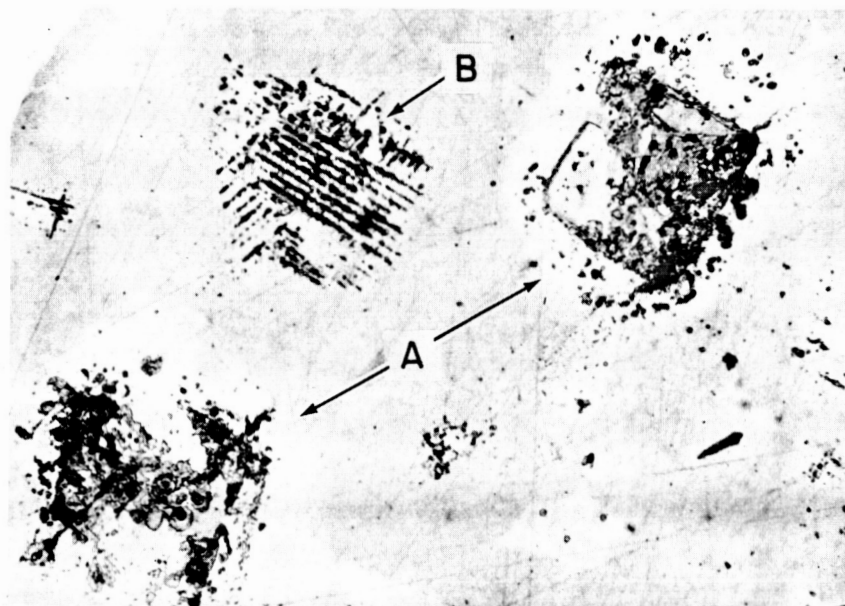


FIG. 3 MICROSTRUCTURE AT SALT CONTACT SPOTS ON PREPOLISHED Ti-8Al-1Mo-1V ALLOY EXPOSED 1 DAY AT YIELD STRESS AT 650°F WITH SEA SALT DEPOSIT. Material was duplex-annealed. Note the tiny cracks and pits at A; a corrosion pattern at B related to crystallographic planes in salt crystal; and that the oxide film is apparently thinner around salt contact spots. 250X

seen by comparison with Figure 10a. This observation may provide some insight to the mechanism of cracking, and will be investigated in more detail in the next quarter. A high resolution autoradiography technique will be used in future tests with salt containing radiotracers ^{22}Na , ^{36}Cl , and ^3H (tritium) to study these initial stages of salt-metal corrosion.

Another interesting feature shown in Figure 3 is that the oxide film on the polished metal surface is lighter (more reflective) at salt contact spots, which implies either that the oxide did not grow as rapidly in these areas, perhaps because of the presence of a reducing atmosphere (HCl gas), or that the oxide was consumed during the salt-metal reaction.

Role of Surface Oxide

The rapid initiation of cracking in polished surfaces and the results of microscopic examination of salt contact spots described above suggested that the initiation of hot-salt cracking may be strongly influenced by the nature of the surface oxide film. Titanium is an extremely reactive metal which is prevented from corroding rapidly in the atmosphere by the formation of a thin protective oxide film. If hot-salt cracking involves chemical reactions with the base metal, either the reactants must diffuse through the oxide, or the oxide film must be dissolved by some reactant or mechanically ruptured. The first two mechanisms seem most likely.

Localized dissolution of the oxide or diffusion through it should depend on its thickness and composition. The thickness and possibly the composition should depend on the temperature at which the oxide is formed. During this quarter studies were begun to determine the effect of heating at various temperatures on the composition of the oxide film and to determine the effect of these oxide films on initiation of stress corrosion cracking.

Preliminary analyses using a spark-source, double-focusing mass spectrometer show that in oxide films formed at 900 and 1100°F, the ratio of aluminum to titanium is quite variable, probably because the instrument examines a very small volume (a sphere of sample 20 microns in diameter). However the average aluminum-to-titanium ratio in the oxide is greater than in the base metal (Table II). This raises the possibility that the initiation and propagation of cracks involves selective attack of alloying elements.

TABLE II

Spark-Source Mass Spectrometer Analyses
of Oxide Film on Ti-8Al-1Mo-1V Alloy

| Temp of Oxide Formation, °F | Time at Temp, hr | Specimen | Ratio ^(a) of Alloy Element to Ti, wt % x 100 | | | | | |
|--------------------------------------|------------------------|----------|---|------|-------|---------------------------|------|-------|
| | | | Oxide | | | Base Metal ^(b) | | |
| | | | Al/Ti | V/Ti | Mo/Ti | Al/Ti | V/Ti | Mo/Ti |
| 900 | 3 | 1 | 19.5 | 0.98 | 0.26 | | | |
| | | 2 | 71.4 | 0.72 | 0.23 | | | |
| | | 3 | 6.7 | 1.24 | 0.66 | | | |
| | | 4 | 102.0 | 74 | 0.34 | | | |
| | | Avg | 50.0 | 0.92 | 0.37 | | | |
| 1100 | 3 | 1 | 56.9 | 0.78 | 0.45 | | | |
| | | 2 | 21.4 | 0.74 | 0.30 | | | |
| | | Avg | 39.2 | 0.76 | 0.38 | 23.1 | 1.21 | 0.51 |

(a) These ratios are calculated assuming that the sensitivity of detection is unity. The sensitivity is not unity, but sensitivity is constant for a given matrix. Therefore, the ratios shown for the base metal can be used as a qualitative reference to determine if a given element is enriched in the oxide.

(b) Average of ratios from 12 individual determinations.

Only one test has been performed to date to determine the effect of oxide film thickness on stress corrosion cracking. A strip of Ti-8Al-1Mo-1V alloy was heated in an oxy-acetylene flame to produce a thin adherent scale. The strip was then cut longitudinally, and one-half was ground and polished. Both pieces were then stressed in the same holder, sea salt was applied, and the holder was placed in a muffle furnace at 650°F for 14 days. After removal of the excess salt, numerous cracks were visible on the polished sample, but the scaled sample had only three tiny cracks near the edge along which the cut was made. These cracks were not visible until the surface scale was removed by light grinding and polishing. The difference in susceptibility to cracking was not due to heating effects on the structure because the polished half received the same heat treatment. This test indicates that a heavy oxide film may protect against initiation of cracking which agrees with previous reports that anodized surfaces resist cracking⁽⁶⁾. These studies are continuing.

Tests using the isotope $^{18}\text{O}_2$ to determine the role of oxygen in the corrosion phenomenon have not been started. Preliminary considerations have indicated that mass spectrometric analyses do not appear to be feasible for tracking the behavior of this nonradioactive isotope. A suitable alternative technique has not yet been developed.

Role of Moisture and HCl Gas

Previous tests⁽¹⁾ using natural sea salt and sea salt containing radiotracer ^{36}Cl provided evidence that a volatile chlorine-bearing product, tentatively identified as HCl gas, is given off when either salt alone or salt-coated chips of titanium alloy are heated at 650°F. The HCl gas presumably is generated during dehydration. During this quarter, confirming evidence was obtained that the product is HCl gas and not volatile metal chlorides.

Thin chips of Ti-8Al-1Mo-1V alloy were placed in a glass boat and 5 ml of saturated sea salt solution was added. The mixture was evaporated to dryness on a warm hot plate at about 200°F. The sample was then placed in a tube furnace at 650°F, and dry air was blown over the sample, through a glass wool filter, and then bubbled through de-ionized water. The water was removed after various times and replaced each time with fresh water. The water samples were analyzed for Cl^- , Na, K, Mg, Ca, Ti, and Al. Significant concentrations of Cl^- were found, but only traces of the metallic elements were present (parts per billion range), indicating that the product must be HCl gas. The concentration of chloride ion was far in excess of that which would be formed by dissociation of chlorine gas in the water. However, this does not preclude the possibility that a trace of chlorine gas was present. The fact that Cl^- was detected when salt alone was heated provides additional evidence that the product is HCl gas.

Most of the HCl gas was given off during the first few hours of heating. This is shown in Figure 4, in which chloride ion concentration expressed as ppm accumulated in the water per hour of air flow is plotted against test time. The apparent sudden release of chloride-bearing product during the second hour of heating will be investigated further to determine the influence of moisture in the salt and in the oxide film and whether this effect is reproducible. It is expected that moisture in the salt plays the major role in determining the quantity of HCl given off. The moisture content is apt to vary among samples, and therefore the quantitative amount of Cl^- accumulated in the water may vary somewhat in multiple tests of the type described above.

Studies are continuing to determine if HCl gas or the resultant NaOH is involved in stress corrosion. Either of these chemicals could selectively attack aluminum in the oxide and base metal. Evidence of NaOH in salt-metal corrosion products was reported by Martin,⁽²⁾ who suggested that NaOH was a product of the corrosion reactions. The SRL evidence suggests that NaOH may be a reactant.

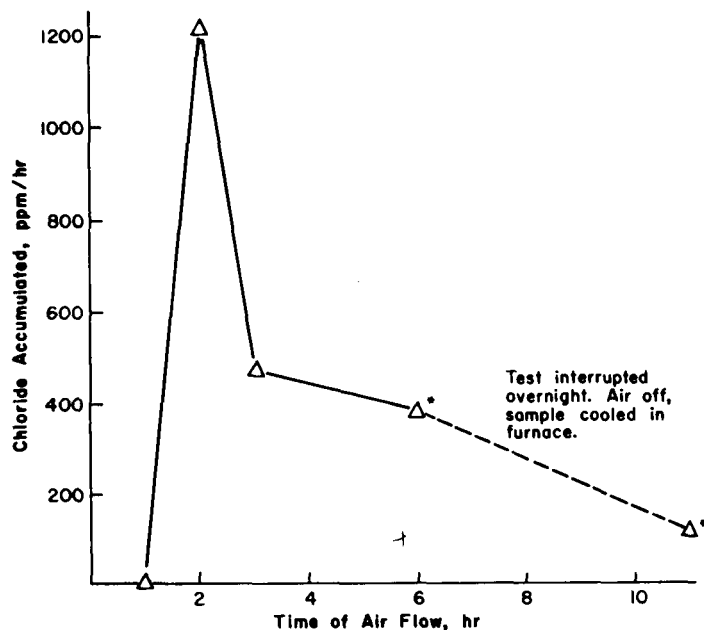


FIG. 4 ACCUMULATION OF CHLORIDE ION IN WATER TRAP IN EFFLUENT AIR STREAM BLOWN OVER SALT-COATED CHIPS OF Ti-8Al-1Mo-1V ALLOY AT 650°F.

*Averages for single water samples used continuously for 3 hours.

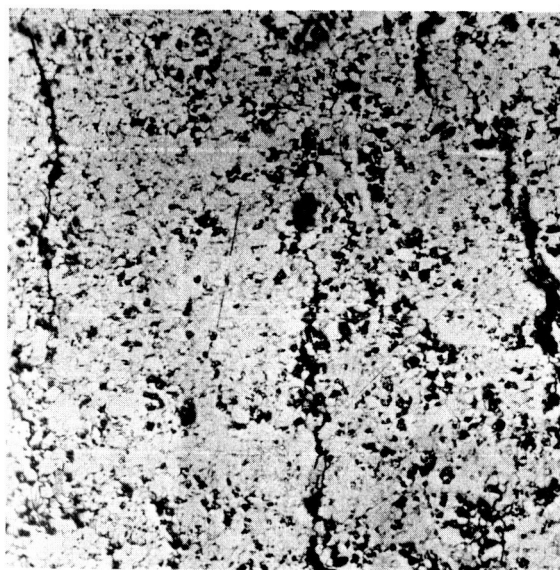
Role of Cations in Salt

Sea salt contains four principal chlorides: NaCl, KCl, $MgCl_2$, and $CaCl_2$. Tests performed during the quarter to determine if cracking behavior is influenced by the cation species revealed that NaCl and KCl are much more aggressive than $MgCl_2$ and $CaCl_2$.

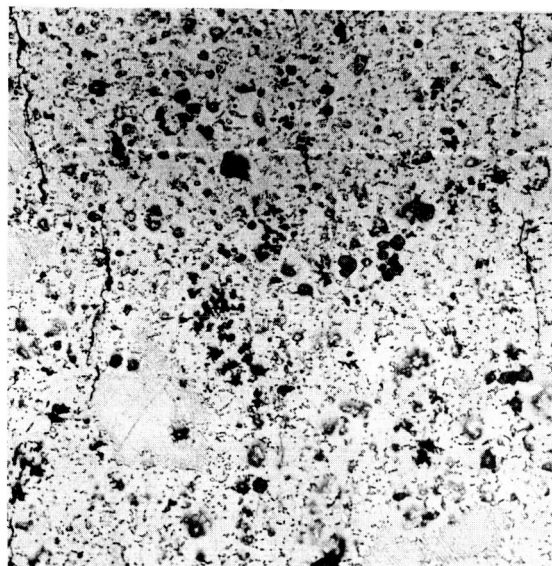
Droplets of saturated solutions of each of these four individual chlorides were dried on polished-and-stressed samples that were subsequently exposed 14 days at 650°F. After exposure, the excess salt was washed off and the sample surfaces were lightly repolished (no grinding) for microscopic examination. As shown in Figure 5, NaCl and KCl caused severe pitting and cracking, while only a few tiny cracks, which were very difficult to find, occurred on samples exposed to $MgCl_2$ and $CaCl_2$.

These results may be related to the strengths of hydroxides of these cations. NaOH and KOH are both strong bases, whereas $Mg(OH)_2$ and $Ca(OH)_2$ are both weak bases.

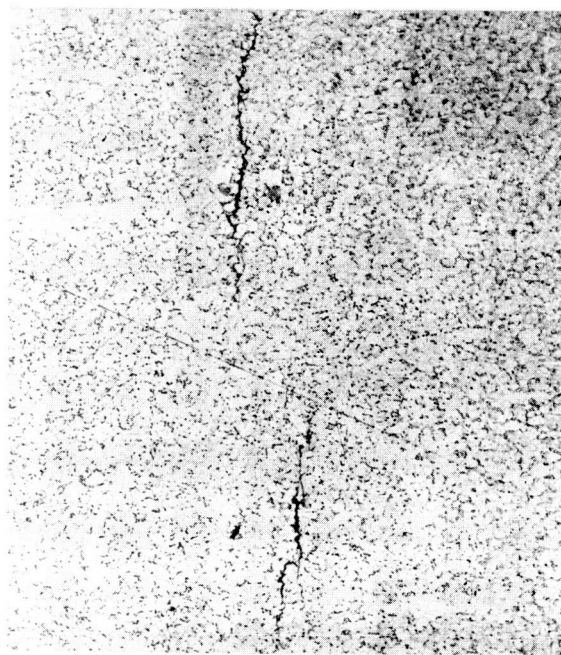
In order to minimize the complexity of reactions and products involved in hot-salt cracking studies, future tests will use only NaCl.



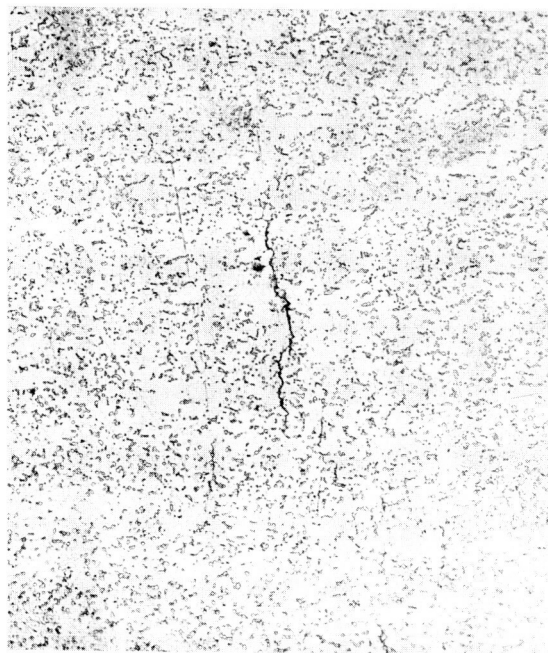
a. NaCl



b. KCl



c. $MgCl_2$



d. $CaCl_2$

FIG. 5 EFFECT OF CATION IN CHLORIDE ON HOT-SALT STRESS CORROSION CRACKING OF Ti-8Al-1Mo-1V ALLOY. Samples were duplex-annealed material (Heat D-5657), prepolished, coated with individual salts indicated above, and exposed 14 days at 650°F at the yield stress. Excess salt removed by washing and repolishing. 250X

Identification of Corrosion Products

Attempts to use X-ray diffraction for identification of corrosion products produced in "salt sandwiches" exposed at various temperatures during the first quarter have been unsuccessful. The "salt sandwich" technique of observing the salt-metal reaction has been abandoned in favor of microscopic examination of salt contact spots on prepolished surfaces.

A hot-stage X-ray diffraction technique is being considered for studies to identify corrosion products generated "in situ."

Tests with Radiotracers ^{36}Cl and ^{22}Na

Radiotracers ^{36}Cl and ^{22}Na are being used in studies of hot-salt corrosion. Traces of both ^{36}Cl and ^{22}Na have been detected by radiation counters in cracked samples after all excess salt and corrosion products were removed by washing, light grinding, and polishing. However, a high-resolution autoradiography technique has not yet been perfected for determining the exact location of these elements with respect to the cracks.

Typical radioactivity counter results are summarized in Table III. The level of radioactivity was quite low after removal of excess salt. The low activity level may be due to removal of soluble chloride and sodium bearing reactants and products during washing. However, the fact that even traces of activity are present after light grinding and polishing indicates that both chloride and sodium are present either in the cracks or in micropits.

TABLE III

Results of Tests Using Radiotracers ^{36}Cl and ^{22}Na

| Exposure, days at 650°F(a) | Salt | Tracer | Beta Radiation Detected, counts per minute | |
|----------------------------------|----------|------------------|---|--|
| | | | Sample Washed | Sample Washed, Reground, and Polished |
| 7 | Sea salt | ^{36}Cl | 5 | - |
| 14 | Sea salt | ^{36}Cl | 30-60 | - |
| 14 | Sea salt | ^{36}Cl | 70 | 20-50 |
| 14 | NaCl | ^{36}Cl | 170 | 12 |
| 7 | NaCl | ^{22}Na | 85 | 20-30 |

(a) Cracks occurred on all samples.

In future tests the excess salt will be removed by dry brushing and scraping so that soluble species can be retained in the corroded areas. Also, the role of hydrogen will be investigated by using ^3H (tritium) in the salt water used to apply the salt deposits.

Effects of Sample Orientation in Rolled Sheet

A limited number of tests were performed to compare the cracking behavior and mechanical properties of strip samples cut parallel to and transverse to the rolling direction of the duplex-annealed Ti-8Al-1Mo-1V alloy sheet (heat D-5657). Sample orientation appeared to have no effect on initiation of cracking in strips with NaCl deposits exposed for various times from 5 hours to 14 days while stressed to the yield stress at 650°F. Tiny cracks were visible after 5 hours in both types. Crack propagation rate was not determined.

Room-temperature tensile tests showed that the mechanical properties and strain anisotropy were approximately the same in the longitudinal and transverse directions. The load-elongation curves for both directions were nearly identical and showed a definite inflection at approximately 9% elongation (Figure 6). Metallographic examination of specimens tested to different points along the load-elongation curve revealed that the inflection corresponded to the initiation of twinning and the start of necking.

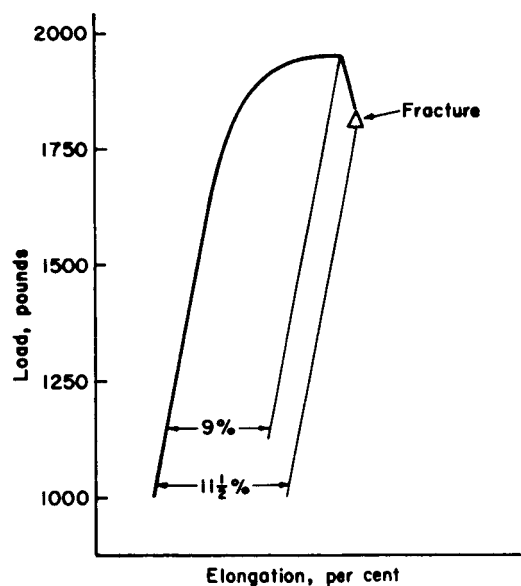
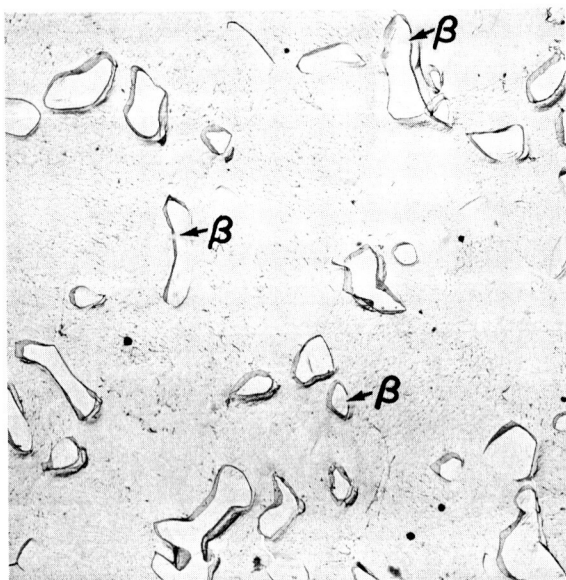


FIG. 6 TYPICAL LOAD-ELONGATION CURVE FOR Ti-8Al-1Mo-1V ALLOY IN THE DUPLEX-ANNEALED CONDITION

Fractography of the rupture surfaces on tensile samples showed that failure occurred predominantly by shear. As shown in Figure 7a and b, comparison of the number of beta phase particles in a metallographic section with the number in the rupture surface indicated that fracture occurred through the alpha matrix with no preferential cracking along beta-alpha phase boundaries or through beta phase particles. This is in contrast to the preference for hot-salt stress corrosion cracking to occur along beta-alpha phase boundaries shown in Figure 10b.



a. Metallographic section. Note the large number of beta particles.

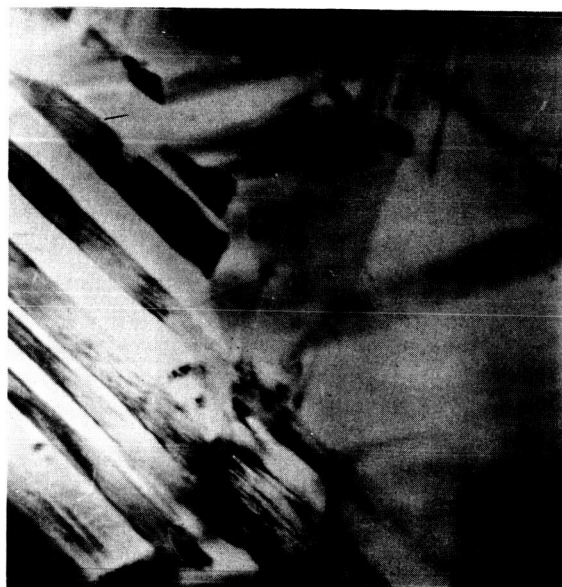


b. Tensile rupture surface. Note that little or no beta phase can be seen. Arrow points to possible beta particle.

FIG. 7 COMPARISON OF BETA PHASE PARTICLES IN METALLOGRAPHIC SECTION AND TENSILE RUPTURE SURFACE. The lack of evidence of beta phase in the tensile rupture indicates that the alloy had no preference for fracture along beta-alpha phase boundaries or through beta particles. 3200X

Electron Microscopy Studies

During this quarter, transmission electron microscopy studies were directed toward further characterization of Ti-8Al-1Mo-1V alloy structure. Thin foils for transmission studies were prepared from the 0.050-inch-thick sheet of duplex-annealed alloy (heat D-5657). The structural appearance of many regions of this material (Figure 8) was similar to that seen previously in foils prepared from the 0.030-inch-thick sheet of mill-annealed alloy (heat D-3420). Selected-area electron diffraction studies revealed that the matrix was the hexagonal alpha phase and that the large second phase particles in the matrix



a.

37,000X



b.

37,000X

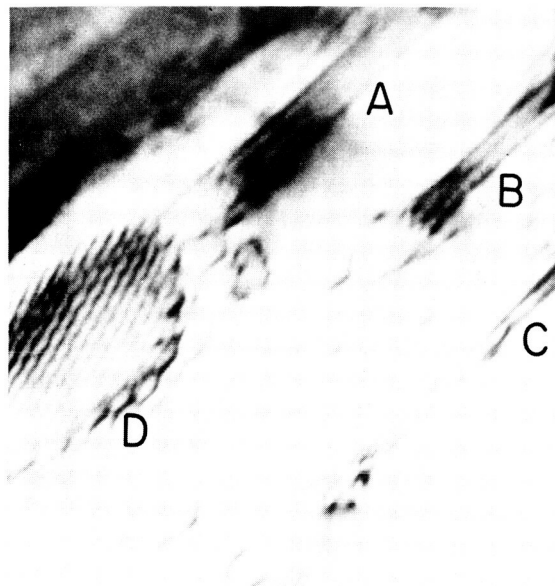
FIG. 8 ELECTRON TRANSMISSION MICROGRAPHS OF Ti-8Al-1Mo-1V ALLOY IN THE DUPLEX-ANNEALED CONDITION



a.

37,000X

Note coplanar array of dislocations at area A



b.

50,000X

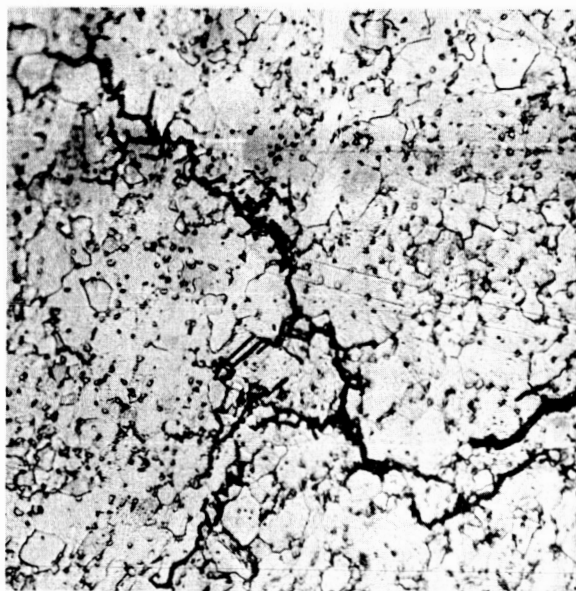
Note stacking faults A,B, and C and the hexagonal dislocation network with extended nodes at D

FIG. 9 DISLOCATIONS IN THE Ti-8Al-1Mo-1V ALLOY IN THE DUPLEX-ANNEALED CONDITION

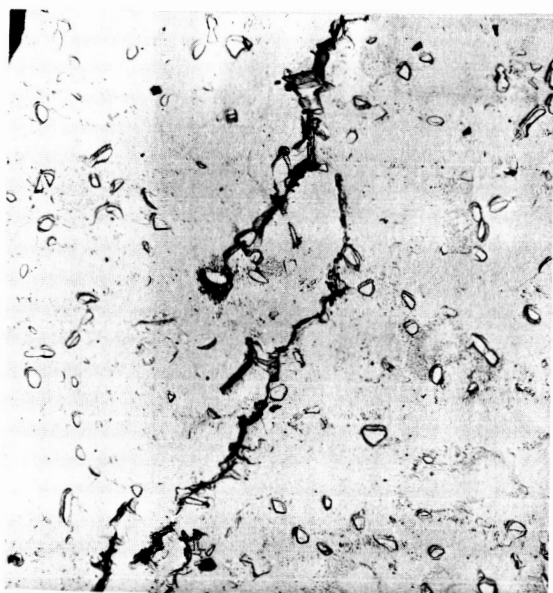
were the body-centered cubic beta phase. Dislocations, dislocation networks, and stacking faults were apparent in many areas in the foil (Figure 9). The observation of coplanar arrays of dislocations (Figure 9a), stacking faults (Figure 9b), and extended nodes in dislocation networks (Figure 9b) suggest that the stacking fault energy of the alloy was quite low. The reasons for the structural contrast in regions such as shown in Figure 8a have not yet been determined; however, it is probable that hydrogen was charged into the samples during foil preparation. Hydride contamination has been shown to produce such contrast effects in titanium alloys⁽³⁾.

During foil preparation, the thinning operation caused preferential attack to occur along the alpha beta phase boundaries and along alpha grain boundaries, as previously reported⁽¹⁾. It is interesting to compare this preferential attack to the mode of attack that occurs during preparation of stainless steel foils.^(4,5) In austenitic stainless steels stress corrosion cracking normally occurs along transgranular paths, and stacking faults and coplanar arrays are believed to be the susceptible paths. Preferential attack occurs along these paths during preparation of thin foils of stainless steel, just as preferential attack and stress corrosion cracking occur along grain and phase boundaries in Ti-8Al-1Mo-1V alloy. This comparison suggests that a corrosion phenomenon plays a major role in crack propagation in both stainless steels and titanium alloys.

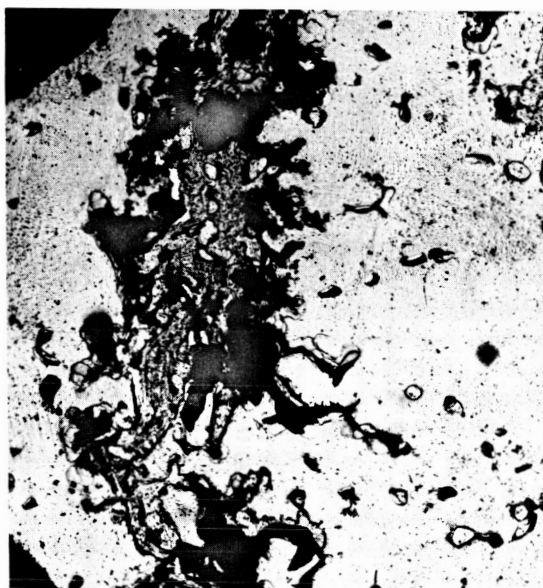
The morphology of hot-salt cracking in a U-bend sample from heat D-3420 exposed to sea salt and air at 1200°F was described previously in some detail.⁽¹⁾ The cracks were filled with corrosion products, presumably an oxide. During the past quarter, cracking was studied in a sample from the same heat of alloy exposed for two weeks to sea salt and air at 650°F. As in the previous sample, the cracks predominantly followed the alpha-beta interfaces and the alpha grain boundaries; however, some indications of transgranular cracking were noted (Figure 10a). The cracks produced at 650°F (Figure 10b) were much finer than those produced at 1200°F (Figure 10c) and little or no oxide was apparent within the cracks. In addition to the formation of hot-salt cracks, the two-week exposure at 650°F produced more of the fine second phase within the alpha grains (see Reference 1 for a discussion of this phase).



a. Cracked at 650°F. Note traces of transgranular cracking. 500X



b. Cracked at 650°F. 1500X



c. Cracked at 1200°F. 1900X

FIG. 10 COMPARISON OF HOT-SALT CRACKS FORMED AT 650 AND 1200°F. Cracks formed at 650°F were finer and contained little or none of the oxide seen in the crack formed at 1200°F

REFERENCES

1. S. P. Rideout, M. R. Louthan, and C. L. Selby. Stress Corrosion Cracking of Titanium Alloys, Progress Report - April 1-June 30, 1964. USAEC Report DP(NASA)-917, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).
2. G. Martin. Investigation of Long Term Exposure Effects Under Stress on Supersonic Transport Structural Alloys. USAEC Report NA-64-658, North American Aviation, Inc., Los Angeles Division, Los Angeles, Calif. (1964).
3. M. J. Blackburn. Private discussion.
4. M. R. Louthan. Stress Corrosion Cracking of Type 304 Stainless Steel, Status Report - March 1, 1964. USAEC Report DP-907, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).
5. P. R. Swann. "Dislocation Substructure vs Transgranular Stress Corrosion Susceptibility of Single Phase Alloys." Corrosion, Vol 19, p. 102t-112t (1963).
6. The Salt Corrosion of Titanium Alloys at Elevated Temperature and Stress - Progress Report. USAEC Report TML-88, Battelle Memorial Inst., Titanium Metallurgical Lab., Columbus, Ohio (1957).